Polymers in Confined Geometries

Characterization of Thin Bilayer Films by NEXAFS Microscopy

Some details of the behavior of thin films of polymer mixtures are difficult to study with conventional characterization techniques because many of these methods are unable to chemically differentiate materials with good spatial resolution and without damage, staining, or preferential solvent washing. In order to achieve direct and quantitative chemical characterization, Harald Ade from North Carolina State University and collaborators from several institutions are using near-edge x-ray absorption fine structure (NEXAFS) microscopy at the Advanced Light Source (ALS) and the National Synchrotron Light Source (NSLS) to investigate the surface and bulk properties of thin films. One of the goals of this research is to investigate the pathways leading to reproducible fabrication of polymer mesostructures and to study their morphological characteristics.

Confining polymer molecules to geometries that are smaller than a few times the molecules' size influences properties such as viscosity and morphology. A polymer thin film on a substrate, where the substrate surface provides a rigid interface and the transition to air a flexible interface, is one of the simplest confined geometries. The interaction of a polymer with the substrate determines, for example, if the polymer film is stable, or if the film has a tendency to dewet the substrate. The dewetting process of a polymer is similar to a water film breaking up into water droplets on a car windshield or a dinner plate. The wetting characteristics of polymers with surfaces and dispersants are commercially important for the effective production of various coatings and films, including dielectric layers, photographic materials, and paints.

Films of polymer blends often exhibit more desirable characteristics than individual homopolymers; however, most blend components are also highly incompatible and will undergo demixing and phase separation. The degree of phase separation in polymer blends can have adverse affects on the properties of the resulting film, owing to changes in morphology. Conversely, a phase-separated film with controlled morphology might exhibit superior characteristics. The controlled thin film morphologies might be used as selective membranes or sensors, or they could be used to produce controlled nanostructures that might have interesting optical or magnetic properties.

Understanding the variables that effect the demixing morphology and to what degree the kinetics and dynamics are influenced are issues of considerable commercial interest. Controllable parameters are the polymer's size (viscosity, diffusivity), polymer and hetero-surface composition (interfacial energies, interaction parameter), additives such as compatibilizers (interfacial energy), and the distance scale, such as film thickness.

Ade and his collaborators used the photoemission electron microscope (PEEM) at ALS Beamline 8.0.1 for NEXAFS microscopy of surfaces and the scanning transmission x-ray microscopes (STXMs) at ALS Beamline 7.0.1 and NSLS Beamline X-1 for NEXAFS microcopy of the bulk in a variety of confined systems. In one study, they investigated the thickness dependence of the dewetting characteristics of annealed bilayers comprising brominated polystyrene (PBrS) on top of polystyrene (PS) on a silicon substrate.

The researchers observed that the PBrS dewets the PS layer upon annealing. The PS even encapsulates the PBrS during the advanced stages of dewetting as the system approaches its thermodynamic equilibrium. The encapsulation process proceeds more slowly as the PS layer thickness is reduced, a direct result of the increased viscosity due to spatial confinement. The researchers observed no encapsulation or only partial encapsulation once the PS layer thickness approached the radius of gyration (a measure of the molecule's size). The decreased encapsulation occurs because the PS is being pinned to the silicon surface, thereby trapping the system in a state far from thermodynamic equilibrium.

This type of research provides the information needed to investigate the pathways leading to reproducible fabrication of polymer nanostructures and to study the morphological characteristics and dynamics of such nanostructures.

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H. Ade, D. A. Winesett, A. P. Smith, S. Anders, T. Stammler, C. Heske, D. Slep, M. H. Rafailovich, J. Sokolov, and J. Stöhr, "Bulk and Surface Characterization of a Dewetting Thin Film Polymer Bilayer," *Appl. Phys. Lett.* **73** (1998) 3775; D. Slep, J. Asselta, M. H. Rafailovich, J. Sokolov. D. A. Winesett, A. P. Smith, H. Ade, and S. Anders, "The Effect of an Interactive Surface on the Equilibrium Contact Angle in Bilayer Polymer Films." Submitted to *Langmuir*.

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- **Polymer thin films and nanostructures**
  - *Thin-films already have considerable technological importance*
    - Coatings (lithography, paints, adhesives, lubricants)
    - Electronics (dielectric insulators, flat-panel and liquid-crystal displays)
  - *Nanostructures with controllable morphologies are coming*
    - Membranes
    - Nanocomposites
    - Sensors
- **Example: multicomponent thin polymer films**
  - *Control of morphology during processing controls function and application*
  - *Important variables*
    - Polymer composition (blends, emulsions/compatibilizers)
    - Interfacial energy (polymer/polymer, polymer/air, polymer/substrate)
    - Size (molecular weight, film thickness)

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D. Slep (Hilord Chemical Corp); J. Asselta, M. H. Rafailovich, and J. Sokolov (SUNY-Stony Brook); D. A. Winesett, A. P. Smith, and H. Ade (North Carolina State University); and S. Anders (ALS). [*Langmuir* 16, 2369 (2000)]

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- **Compositional mapping is important tool**
  - *Natural length scale: molecular “diameter” (radius of gyration) tens of nm*
  - *NEXAFS microscopy provides high spatial resolution*
  - *Bulk composition with the scanning transmission x-ray microscope (STXM)*
  - *Surface composition with the photoemission electron microscope (PEEM)*

- **Dewetting bilayers and phase-separating blends**
  - *Brominated polystyrene/polystyrene (PBrS/PS) model system*
  - *Combined surface and bulk measurements give encapsulation pathways and qualitative dynamics*
  - *Determined for films with thicknesses up to 150 nm*
  - *PBrS encapsulated during dewetting only if PS film thickness is larger than the radius of gyration*

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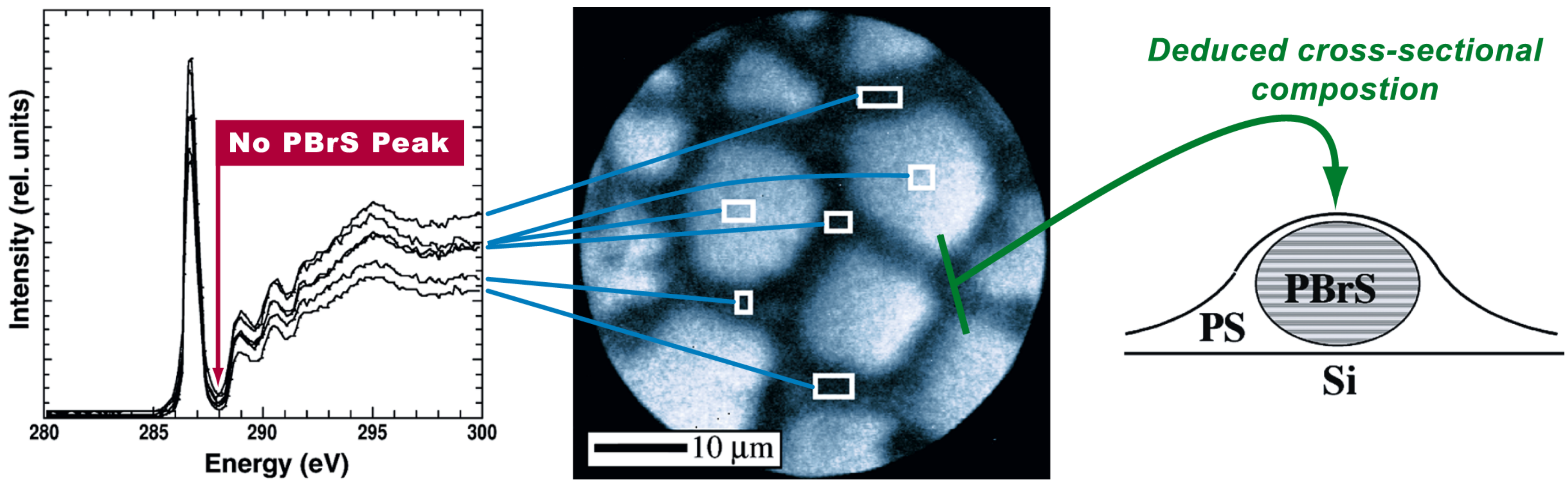

NEXAFS spectra from boxes in PEEM image; only PS is on the surface.

PEEM image showing advanced stages of dewetting via topo-graphy contrast.

Schematic of the deduced morphology across "spines" in image (PBrS detected with STXM).

Morphology of a PBrS film 30-nm thick dewetting from a 34-nm PS thin-film substrate exhibits encapsulation of the PBrS and formation of "spines" prior to breakup into PBrS droplets.

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